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(54) Title: FABRIC TREATMENT COMPOSITION, METHOD OF TREATING FABRIC AND PERFLUOROALKYL
AMPHIPHILIC COMPOUNDS

(57) Abstract: Compounds of general formula (I): $R_f-A-C(O)-N(R)-CH_2-(CHOH)_xCH_2OH$, wherein: R_f is a group of formula (II): $(C_mX_{2m+1})-$, where m is an integer in the range 3-12, preferably 6-10 and X is a halogen atom, wherein at least 50 % of the halogen atom X are fluorine atoms and the remainder are chlorine or bromine atoms, A is a divalent linking group, and R is a hydrogen atom or a C_1 - C_{18} alkyl or alkenyl group, are used to give oil, soil and water repellency to fabric. They can be used in fabric treatment compositions. Compositions according to general formula (I) but in which R is a C_1 - C_{18} alkyl or alkenyl group are novel compounds.

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FABRIC TREATMENT COMPOSITION, METHOD OF TREATING FABRIC AND PERFLUOROALKYL AMPHIPHILIC COMPOUNDS

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The present invention relates to a fabric treatment composition comprising a perfluoroalkyl amphiphilic compound. The present invention also relates to a method
10 of treating fabric using a perfluoroalkyl amphiphilic compound. The present invention further provides a novel class of perfluoroalkyl amphiphilic compounds. The present invention further provides a method of synthesising perfluoroalkyl amphiphilic compounds for use in fabric
15 treatment.

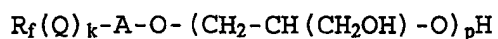
The present invention is concerned with fabric treatment. The fabric treatment may be treatment before use, for example during the manufacture of fabric or garments, or it
20 may take place after use of the fabric. Fabric treatment that takes place after use of the fabric, here termed fabric care, is used to reverse degradation of fabric that occurs as a result of use of the fabric, for example soiling and staining. Such treatments include laundering
25 and the application of non-laundry fabric care products, such as spray-on products.

Considerable attention has been focused on components for inclusion in laundry and non-laundry compositions, which
30 are specifically intended for fabric care. For example, colour care components such as photofading inhibitors and fluorescence inhibitors have been provided. Fabric softening components can be used. Soil release polymers

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are sometimes included in fabric care compositions which are deposited onto the fabric to allow soil and stains to be more easily removed during laundering.

- 5 EP-A-0240601 (Hoechst) discloses perfluoroalkyl polyglycerine compounds of general formula A:



- 10 wherein R_f is a perfluoro alkyl moiety, Q is a divalent linking group, K is 0 or 1, A is an alkenylene or divalent aryl linking group and p is 1-15.

- 15 These compositions can be used to give oil and soil repellency to textiles, leather, wood or paper.

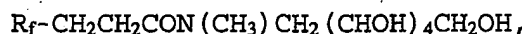
- Compounds of formula A are amphiphilic - the polyglycerine chain has hydrophilic properties whereas the perfluoroalkyl
20 moiety has hydrophobic properties.

- Compounds of general formula A include an ether group between the polyglycerine chain and the rest of the molecule. Such ether bonds can be difficult to synthesise
25 in practice.

- EP-A-0255443 (ATTA) discloses surfactants, typically for use in pharmaceutical preparations, having a polyhydroxylated hydrophilic moiety, a highly fluorinated
30 moiety and a functional junction group linking the moieties together.

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Included in the disclosure of EP-A-0255443 are compounds of general formula B:



B

5

wherein $R_f = C_5F_{11}$, C_7F_{15} or C_8F_{17}

However, there is no mention that these compounds may have any application in the treatment of fabrics.

10

EP-A-0255443 further discloses a process for preparation of the compounds thereof. The process involves reacting a polyol or aminopolyol in which the hydroxy groups, or part thereof, are protected, with a highly fluorinated derivative so as to link the polyol or aminopolyol moiety with the highly fluorinated moiety through a functional junction group. The highly fluorinated derivative may be an alcohol, an amine, an anhydride, a mixed anhydride or an acyl chloride. Compounds of general formula B are synthesised by reacting glucamide with an acid anhydride derivative of the highly fluorinated moiety.

15
20

The present invention sets out to provide fabric treatment compositions which use perfluoroalkyl amphiphilic compounds which are easy to synthesise and which give water, soil and oil repellency to fabric. The present invention further sets out to provide perfluoroalkyl amphiphilic compounds which are simple to synthesise.

25

Accordingly, in one aspect, the present invention provides fabric treatment compositions comprising a perfluoroalkyl amphiphilic compound of general formula (I):

30

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wherein:

5 R_f is a group of the formula (II):



where m = an integer in the range 3-20, preferably
10 4-18, and X is a halogen atom, wherein at least 50% of
the halogen atom X are fluorine atoms and the reminder
are chlorine or bromine atoms,

15 A is a divalent linking group, and

R is a hydrogen atom or a C_1 - C_{18} alkyl or alkenyl
group.

The present inventors have discovered that perfluoroalkyl
20 glucamides are relatively easy to synthesise because of the
amide bond. However, the amide bond is found to be stable
on storage. The compounds are found to give excellent soil
and oil repellency to cotton and polyester fabrics, and
water repellency to polyester fabrics.

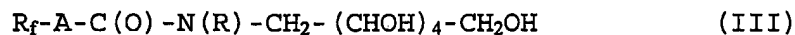
25 In another aspect, the present invention provides the use
of a perfluoroalkyl amphiphilic compound according to
general formula (I) above in a method of polyester fabric
treatment, to give oil, soil and water repellency to the
30 polyester fabric.

In a further aspect, the present invention provides the use
of a perfluoroalkyl amphiphilic compound according to

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general formula (1) above in a method of cotton fabric treatment, to give oil and soil repellency to the cotton fabric.

- 5 In another aspect, the present invention provides a method of treating a fabric comprising applying a fabric treatment composition comprising the perfluoroalkyl amphiphilic compound of general formula (I) above to the fabric.
- 10 In another aspect, the present invention provides a perfluoroalkyl amphiphilic compound of general formula (III):



15

wherein R_f and A have the meanings given in relation to general formula (I) above and R is a C_1 - C_{18} alkyl or alkenyl group.

- 20 In another aspect of the present invention, there is provided a method of synthesising the perfluoroalkyl compound of general formula I comprising the step of reacting with N-alkyl glucamine a compound of general formula (IV);

25



wherein R_f , A have the meanings given in relation to general formula I above and R_1 is an alkyl group.

30

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Detailed Description of the Invention

Preferred aspects of the present invention will be described below.

5

Perfluoroalkyl Amphiphilic Compounds

Any suitable perfluoroalkyl amphiphilic compound falling within general formula I above may be used. However, the following features are particularly preferred.

10

Preferably, the perfluoroalkyl group R_f is a highly fluorinated moiety wherein at least 50% of the atoms bonded to the carbon skeleton are fluorine atoms, the other atoms bonded to the carbon skeleton being hydrogen, chlorine or bromine atoms. Preferably, there are at least four fluorine atoms.

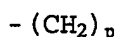
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The perfluoroalkyl group R_f is preferably of general formula C_qF_{2q+1} or $C_qF_{2q}Cl-$, wherein q is an integer in the range 3-12. It is preferred that q is in the range 4-12, more preferably 6-12, most preferably 8-10.

20

The divalent linking group A is preferably selected from C_1-C_{18} alkylene, 1,4 phenylene or 1,4 phenylene substituted with at least one group selected from C_1-C_{18} alkyl, C_1-C_{18} alkoxy, halogen (preferably F) or $-SO_3Na$ the C_1-C_{18} alkylene chains or 1,4 phenyl chains being optionally interrupted by $-O-$. Particularly preferred linking groups are alkylene groups of general formula (V):

30



(V)

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where p is in the range 2-18, more preferably 2-12.

The perfluoroalkyl amphiphilic compounds for use in the present invention may be straight chain perfluoroalkyl glucamides (where R=H or methyl) or branched perfluoroalkyl glucamides, where R is an alkyl group. Straight chain perfluoroalkyl glucamides are known from EP-A-0255443, but branched chain perfluoroalkyl glucamides are novel and a further subject of the present invention.

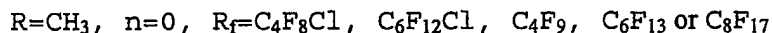
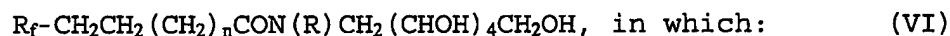
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In general formula (I), R is an alkyl or alkenyl group, which is suitably straight but may be branched. It may have from 1-18 carbon atoms, more preferably 1-12 carbon atoms, and most preferably 1-8 carbon atoms. It may be substituted, for example with OH or halogen atoms.

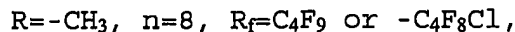
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Particularly preferred perfluoroalkyl glucamides of use in the present invention comprise perfluoroalkyl glucamides of general formula (VI):

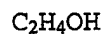
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The last class are novel compounds according to the present invention.

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Method of Preparation of Perfluoroalkyl Glucamides

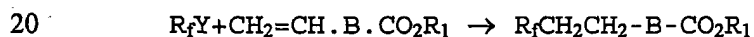
Perfluoroalkyl glucamides according to the present invention may be manufactured by the process disclosed in
5 EP-A-0255443. Alternatively, the novel method of synthesis of the present invention may be used.

The novel synthesis route according to the present invention employs an amidation reaction between an ester
10 derivative of a perfluoroalkyl compound and N-alkyl glucamine.

Suitable ester derivatives can be obtained by any suitable method. Preferably, ester derivatives are methyl esters.

15

The ester derivatives may however be obtained by reacting a perfluoroalkyl halide with an alkenoic acid ester under suitable conditions:



wherein R_f has the meaning given above

B is a linking group which may be selected from the
25 same group from which linking group A is selected, and

R_1 has the meaning set out above.

Preferably, R_1 is methyl. Preferably, the linking group B
30 is $-(CH_2)_n-$, wherein n is in the range 0-16, preferably 0-10.

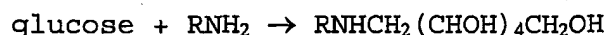
Y is a halogen atom, preferably iodine.

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Halogen derivatives of perfluoroalkyl groups are available in the art and can be obtained from Acros Organics or Fisher Scientific Company.

- 5 N-alkyl glucamines are available in the art from Aldrich Company.

Alternatively, they can be synthesised by reducing glucose in the presence of primary amine. For example, the
10 following reaction may be used:



wherein R has the meaning set out above.

15

The reduction is suitably carried out by hydrogenation in the presence of a suitable catalyst, for example Raney Nickel.

20

Fabric Care Compositions

The present invention is suitable for use in industrial or domestic fabric wash compositions, fabric conditioning
25 compositions and compositions for both washing and conditioning fabrics (so-called through the wash conditioner compositions). The present invention can also be applied to industrial or domestic non-detergent based fabric care compositions, for example spray-on
30 compositions.

Perfluoroalkyl amphiphilic compounds are suitably present in the fabric care compositions of the present invention at

- 10 -

levels in excess of 0.2% by weight, preferably greater than 0.4% by weight. They are preferably present at levels less than 1.5% by weight and preferably less than 1.2% by weight.

5

Fabric Wash Compositions

Fabric wash compositions according to the present invention may be in any suitable form, for example powdered, tableted
10 powders, liquid or solid detergent bars.

Fabric wash compositions according to the present invention comprise a fabric wash detergent material selected from non-soap anionic surfactant, nonionic surfactants, soap,
15 amphoteric surfactants, zwitterionic surfactants and mixtures thereof.

Suitable anionic surfactants are well known to the person skilled in the art and include alkyl benzene sulphonate,
20 primary and secondary alkyl sulphates, particularly C₈-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates, dialkyl sulphasuccinates; ether carboxylates; isethionates; sarcosinates; fatty acid ester sulphonates and mixtures
25 thereof. The sodium salts are generally preferred.

Nonionic surfactants are also well known to the person skilled in the art and include primary and secondary alcohol ethoxylates, especially C₈-C₂₀ aliphatic alcohol
30 ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohol ethoxylated with an average of from 1 to 10 moles of ethylene oxide per

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mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamide). Mixtures of nonionic surfactant may be used.

5

Detergent compositions suitable for use in domestic or industrial automatic fabric washing machines generally contain anionic non-soap surfactant or nonionic surfactant, or combinations of the two in suitable ratio, as will be
10 known to the person skilled in the art, optionally together with soap.

Many suitable detergent-active compounds are available and fully described in the literature, for example in "Surface-
15 Active Agents and Detergents", Volumes I and II, by Schwartz, Perry & Berch.

Anionic surfactant is suitably present at a level of from 5 wt% to 50 wt%, preferably 10 wt%-40 wt% based on the fabric
20 treatment composition. Nonionic surfactant is suitably present at a level of 1-20 wt%, preferably 5-15 wt%.

The total amount of surfactant present will depend upon the intended end use and may be as high as 60 wt% for example
25 in a composition for washing fabrics by hand. In compositions for machine washing of fabric, an amount of from 5 to 40 wt% is generally appropriate.

Detergency Builder

30

The detergent compositions of the invention will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will

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suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

Inorganic builders that may be present include sodium
5 carbonate, if desired in combination with a crystallisation
seed for calcium carbonate, as disclosed in GB 1 437 950
(Unilever); crystalline and amorphous aluminosilicates,
for example, zeolites as disclosed in GB 1 473 202 (Henkel)
and mixed crystalline/amorphous aluminosilicates as
10 disclosed in GB 1 470 250 (Procter & Gamble); and layered
silicates as disclosed in EP 164 514B (Hoechst). Inorganic
phosphate builders, for example, sodium orthophosphate,
pyrophosphate and tripolyphosphate are also suitable for
use with this invention.

15
The detergent compositions of the invention preferably
contain an alkali metal, preferably sodium, aluminosilicate
builder. Sodium aluminosilicates may generally be
incorporated in amounts of from 10 to 70% by weight
20 (anhydrous basis), preferably from 25 to 50 wt%.

The alkali metal aluminosilicate may be either crystalline
or amorphous or mixtures thereof, having the general
formula:

25



These materials contain some bound water and are required
to have a calcium ion exchange capacity of at least 50 mg
30 CaO/g. The preferred sodium aluminosilicates contain 1.5-
3.5 SiO₂ units (in the formula above). Both the amorphous
and the crystalline materials can be prepared readily be

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reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange
5 detergency builders are described, for example, in GB 1 429
143 (Procter & Gamble). The preferred sodium
aluminosilicates of this type are the well-known
commercially available zeolites A and X, and mixtures
thereof.

10

The zeolite may be the commercially available zeolite 4A
now widely used in laundry detergent powders. The zeolite
builder incorporated in the compositions of the invention
may be maximum aluminium zeolite P (zeolite MAP) as
15 described and claimed in EP 384 070A (Unilever). Zeolite
MAP is defined as an alkali metal aluminosilicate of the
zeolite P type having a silicon to aluminium ratio not
exceeding 1.33, preferably within the range of from 0.90 to
1.33, and more preferably within the range of from 0.90 to
20 1.20.

Especially preferred is zeolite MAP having a silicon to
aluminium ratio not exceeding 1.07, more preferably about
1.00. The calcium binding capacity of zeolite MAP is
25 generally at least 150 mg CaO per g of anhydrous material.

Organic builders that may be present include
polycarboxylate polymers such as polyacrylates,
acrylic/maleic copolymers, and acrylic phosphinates;
30 monomeric polycarboxylates such as citrates, gluconates,
oxydisuccinates, glycerol mono-, di- and trisuccinates,
carboxymethyloxysuccinates, carboxymethyloxymalonates,
dipicolinates, hydroxyethyliminodiacetates, alkyl- and

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alkenylmalonates and succinates,; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

- Especially preferred organic builders are citrates,
5 suitable used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.
- 10 Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Bleach Components

- 15 Detergent compositions according to the invention may also suitably contain a peroxy bleach system for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.
- 20 Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate,
25 and sodium percarbonate.

- Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising
30 sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

The compositions may further comprise a photobleach system as described, for example, in EP-A-0035470.

Fabric Softening Composition

The fabric treatment composition of the present invention
5 may be a fabric conditioning composition or it may comprise fabric conditioner.

Fabric Softening Compound

10 The fabric softening compound is preferably a cationic nonionic or anionic fabric softening compound.

The fabric softening compound may be a quaternary ammonium material comprising a polar head group and one
15 or two alkyl or alkenyl chains. The fabric softening compound may also be a nonionic fabric softening compound such as a fabric softening oil, a fabric softening silicone composition or a fabric softening ester composition such as sugar esters.

20 Particularly preferably, the fabric softening compound has two long chain alkyl or alkenyl chains with an average chain length greater than C_{14} , more preferably each chain has an average chain length greater than C_{14} ,
25 more preferably at least 50% of each long chain alkyl or alkenyl group has a chain length of C_{18} .

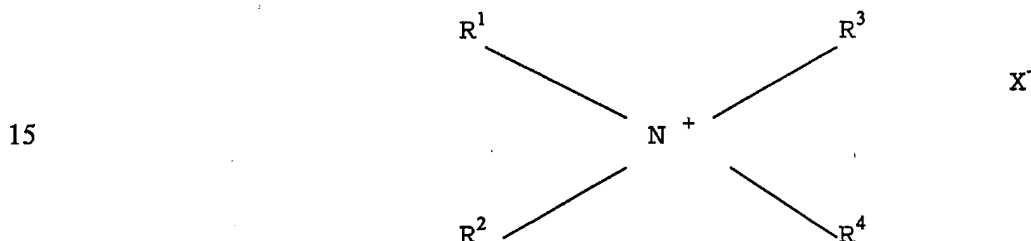
It is preferred if the long chain alkyl or alkenyl groups of the fabric softening compound are predominantly
30 linear.

It is highly preferred if the fabric softening compounds are substantially water-insoluble. Substantially

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insoluble fabric softening compounds in the context of this invention are defined as fabric softening compounds having a solubility less than 1×10^{-3} wt% in demineralised water at 20°C, preferably the fabric softening compounds have a solubility less than 1×10^{-4} , most preferably the fabric softening compounds have a solubility at 20°C in demineralised water from 1×10^{-3} to 1×10^{-6} .

10 Well known species of substantially water-insoluble quaternary ammonium compounds having the formula:



wherein R^1 and R^2 represent hydrocarbyl groups having from 12 to 24 carbon atoms; R^3 and R^4 represent hydrocarbyl groups containing 1 to 4 carbon atoms; and X is an anion, preferably selected from halide, methyl sulphate and ethyl sulphate groups are preferred.

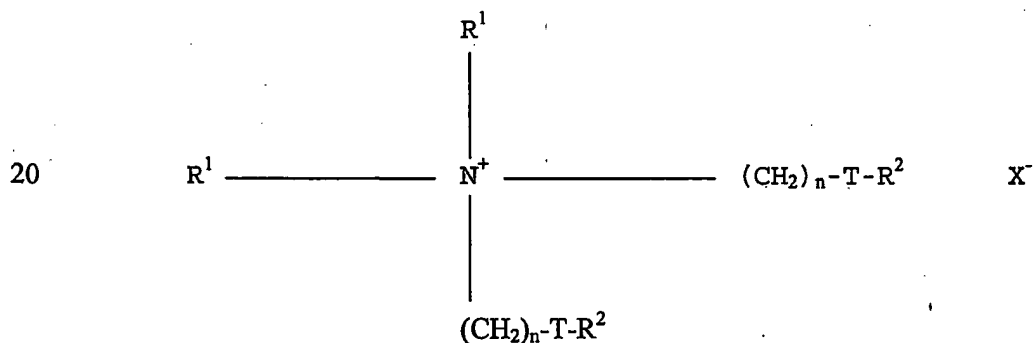
25 Representative examples of these quaternary softeners include di(tallow alkyl) dimethyl ammonium methyl sulphate; dihexadecyl dimethyl ammonium chloride; di(hydrogenated tallow alkyl) dimethyl ammonium chloride; dioctadecyl dimethyl ammonium chloride; di(hydrogenated
30 tallow alkyl) dimethyl ammonium methyl sulphate; dihexadecyl diethyl ammonium chloride; di(coconut alkyl) dimethyl ammonium chloride, ditallow alkyl dimethyl

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ammonium chloride and di(hydrogenated tallow alkyl)
dimethyl ammonium chloride (Arquad 2HT Trade Mark).

Other preferred softeners contain esters or amide links,
5 for example those available under the trade names
Accosoft 580, Varisoft 222, and Stepantex.

Particularly preferred fabric softening compounds are
water-insoluble quaternary ammonium materials which
10 comprise a compound having two C₁₂₋₁₈ alkyl or alkenyl
groups connected to the molecule via at least one ester
link. It is more preferred if the quaternary ammonium
material has two ester links present. The preferred
ester-linked quaternary ammonium material for use in the
15 invention can be represented by the formula:

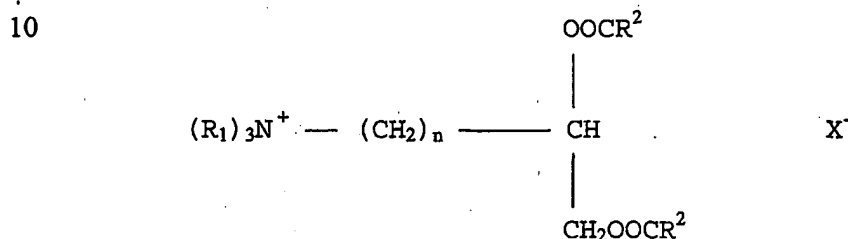


25 wherein each R¹ group is independently selected from C₁₋₄
alkyl, hydroxyalkyl or C₂₋₄ alkenyl groups; and wherein
each R² group is independently selected from C₈₋₂₈ alkyl or
alkenyl groups;

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$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-O-} \end{array}$ or $\begin{array}{c} \text{O} \\ \parallel \\ \text{-O-C-} \end{array}$; X⁻ is any suitable anion and n is an integer from 0-5. Particularly preferred is di(ethyl ester) dimethyl ammonium chloride (DEEDMAC).

A second preferred type of quaternary ammonium material can be represented by the formula:



wherein R₁, n, X⁻ and R₂ are as defined above.

It is advantageous for environmental reasons if the quaternary ammonium material is biologically degradable.

Preferred materials of this class such as 1,2 bis[hardened tallowoxyloxy]-3-trimethylammonium propane chloride and their methods of preparation are, for example, described in US 4 137 180 (Lever Brothers). Preferably these materials comprise small amounts of the corresponding monoester as described in US 4 137 180 for example 1-hardened tallowoxyloxy-2-hydroxy trimethylammonium propane chloride.

The fabric softening agent may also be a polyol ester quat (PEQ) as described in EP 0 638 639 (Akzo).

Other Ingredients

The compositions of the invention can also contain one or more optional ingredients, selected from pH buffering
5 agents, perfume carriers, fluorescers, colorants, hydrotropes, antifoaming agents, antiredeposition agents, enzymes, optical brightening agents, opacifiers, anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-corrosion agents,
10 drape imparting agents, antistatic agents and ironing aids.

The present invention may be in the form of a dilute or concentrated aqueous solution or suspension, for example as described in WO 97/15651, WO 95/27769. Alternatively, the
15 fabric softening composition may be in the form of a powder for use in the rinse cycle of an automatic washing machine. Alternatively, the fabric softening composition may be in the form of a sheet comprising fabric conditioning compositions for use in a tumble dryer, for example as
20 disclosed in WO 95/27777.

Fabric wash detergent compositions according to the present invention may further include through the wash softening material, such as cationic fabric softener.

25

Non-Detergent-Based Fabric Care Products

The present invention can also be used in non-detergent-based fabric care products. For example, the product may
30 comprise the stain removal system as the principal ingredient. For example, non-detergent based compositions may comprise solutions of the stain removal system of the present invention in a suitable solvent, such as isopropanol, alcohol etc. The compositions may comprise

- 20 -

aerosol or spray-on compositions. They may be in the form of sticks, bars, dab-on compositions, for example absorbed into sponges for application to the surface etc.

- 5 The present invention will be further described by way of example only with reference to the following examples.

Examples

- 10 Reference example 1 - preparation of N- alkyl glucamine
RNHCH₂(CHOH)₄CH₂OH

- A solution of D-glucose (50 mmol), an alkylamine (55 mmol) and Raney Nickel (3 grams) in 160 ml of methanol was
15 hydrogenated at 11 atm pressure and 60°C for 12 hours. The Raney Nickel catalyst was removed by filtration and the solution was concentrated to crystalise out the product.

- The results for different alkylamines are set out in Table
20 1 below.

R	Yield (%)	MP (°C)
C ₃ H ₇	75	140-141
C ₄ H ₉	77	129-130
C ₆ H ₁₃	79	126-127
C ₈ H ₁₇	70	121-123
C ₁₀ H ₂₁	72	122-123
C ₁₂ H ₂₅	46	123-126

Reference Example 2 - General Preparative Method for N-alkyl perfluoro alkylglucamide ($R_fCH_2CH_2CON(R)CH_2(CHOH)_4CH_2OH$)

N-alkyl glucamine ($RNHCH_2(CHOH)_4CH_2OH$) in 10 ml anhydrous
5 CH_3OH was heated to 70-80°C in a nitrogen atmosphere before
addition of $R_fCH_2CH_2COOCH_3$ and $NaOCH_3$ (0.05 mmol, 0.955 M).
Reaction was continued at 70-80°C for 20 hours. Additional
methanol was added to dissolve the solids. Then, Dowex
(trade mark) resin (H^+) was added and stirred for 30
10 minutes. After removal of the resin and solvent, the
residue was purified by column chromatography (eluted with
trichloromethane, followed by a 1:9 by volume mixture of
methanol and trichloromethane). Further purification by
recrystallisation yielded products as white solids.

15

Test method - oil repellency

In order to evaluate oil repellency, the following test was
used. Polyester and cotton test cloths of size 4.0 cm x
20 4.0 cm were used.

Polyester was pre-treated with 1N Na_2CO_3 and boiled for 15
minutes. It was then washed with distilled water until
neutral. It was boiled again in distilled water for 15
25 minutes, after which it was dried in a 65°C oven for 30
minutes.

The cotton cloth was treated similarly except that it was
boiled for 30 minutes with sodium carbonate instead of 15
30 minutes.

The test cloths were then each immersed in a methanol or
ethanol solution of perfluoroalkyl glucamide for 1 hour and

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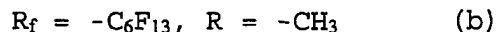
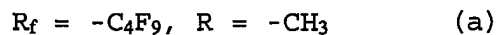
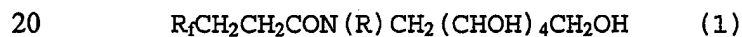
then taken out of the methanol or ethanol solution and dried at 40°C for 30 minutes.

Oil repellency was measured at 15°C using a red-coloured
5 oil (cooking oil flavoured with chilli). A 0.01 ml oil droplet was applied to the treated fabric surface. Effectiveness of repellency was assessed by determining how quickly the droplet spread.

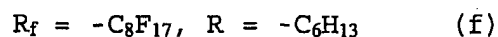
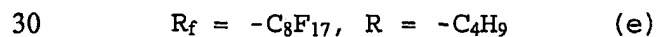
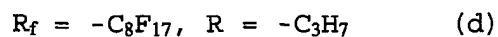
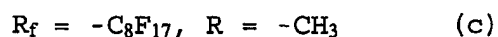
10 There is no repellency if the droplet permeates the fabric quickly. The fabric has weak repellency if the droplet spreads slowly and high repellency if the droplet maintains a high contact angle.

15 Results

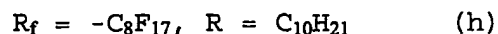
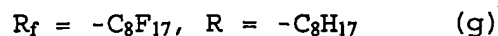
The synthesis methods were used to synthesise compounds according to the following formulae:



25



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- 5 Oil repellency of fabric treated with various quantities of the compounds was tested on polyester and cotton fabric. Results for compounds 1a and 1c are shown in Tables 2 and 3.

10 Table 2 Oil Repellency of Polyester Fabric Treated with
 $R_fCH_2CH_2CON(CH_3)CH_2(CHOH)_4CH_2OH$ (1a-1c)

R _f	C ₄ F ₉ (a)			C ₆ F ₁₃ (b)			C ₈ F ₁₇ (c)		
	0.2	0.5	1	0.2	0.5	1	0.2	0.5	1
Oil repellency	weak	high	high	weak	high	high	high	high	high

15 Table 3 Oil Repellency of Cotton Fabric Treated with
 $R_fCH_2CH_2CON(CH_3)CH_2(CHOH)_4CH_2OH$ (1a-1c)

R _f	C ₄ F ₉ (a)			C ₆ F ₁₃ (b)			C ₈ F ₁₇ (c)		
	0.2	0.5	1	0.2	0.5	1	0.2	0.5	1
Oil repellency	none	weak	weak	weak	high	high	high	high	high

- 20 The results show that high oil repellency can be obtained on polyester fabric with all of the compounds when they are deposited from a 0.5 or 1 wt% solution in methanol. The oil repellency effect is greater for the longer chain length perfluoroalkyl group. High oil repellency can be obtained with compounds having longer perfluoroalkyl chains

on cotton. Perfluoroalkyl chains with greater than 6 carbon atoms are preferred.

The results at various concentrations for compounds (d) -
 5 (g) are shown in Table 4 and 5 which demonstrate the effect of the chain length of the alkyl group substituted on the nitrogen atom.

Table 4 Oil Repellency of Polyester Fabrics with

10 $C_8F_{17}CH_2CH_2CON(R)CH_2(CHOH)_4CH_2OH$

R	Compound	$C_8F_{17}CH_2CH_2CON(R)CH_2(CHOH)_4CH_2OH$ wt% in EtOH			
		0.05%	0.1%	0.2%	0.5%
CH ₃	c	None	Weak	High	High
C ₃ H ₇	d	None	Weak	Weak	High
C ₄ H ₉	e	None	None	Weak	High
C ₆ H ₁₃	f	None	None	None	High
C ₈ H ₁₇	g	None	None	None	High
C ₁₀ H ₂₁	h	None	None	None	Weak

Table 5 Oil Repellency of Cotton Fabrics with
 $C_8F_{17}CH_2CH_2CON(R)CH_2(CHOH)_4CH_2OH$

R	Compound	$C_8F_{17}CH_2CH_2CON(R)CH_2(CHOH)_4CH_2OH$ wt% in EtOH			
		0.05%	0.1%	0.2%	0.5%
CH ₃	c	None	Weak	High	High
C ₃ H ₇	d	None	Weak	High	High
C ₄ H ₉	e	None	Weak	High	High
C ₆ H ₁₃	f	None	Weak	High	High
C ₈ H ₁₇	g	None	Weak	High	High
C ₁₀ H ₂₁	h	None	Weak	Weak	High

- 5 The results demonstrate that weak oil repellency can be obtained with a wide variety of chain lengths over a variety of concentrations of compound in ethanol. High oil repellency can be obtained with N-substituted alkyl chain lengths of 8 or below at 0.5% compound in ethanol. Even
 10 better results are obtained with cotton.

For comparison, the oil repellency test was carried out with the following compounds which are not according to the invention:

15

fluorocarbon surfactant - $C_8F_{17}SO_3K$

linear alkyl benzene sulphonate

20

alkyl glucamide $C_7H_{15}CON(CH_3)CH_2(CHOH)_4CH_2OH$ (MEGA)

Different solvents had to be used in order to dissolve the reference samples to treat the fabric uniformly. The results are shown in Table 6.

5 Table 6 Oil Repellency of Polyester Fabric Treated with Reference Samples

Samples	C ₈ F ₁₇ SO ₃ K			LAS			MEGA	
Solvents	CH ₃ COCH ₃			EtOH:H ₂ O (1:1 v/v)			EtOH	
Sample wt%	0.6	1.2	2.5	0.28	1.1	2.2	0.2	0.6
Oil repellency	none	none	weak	none	none	none	none	none

- 10 It can be seen that LAS and MEGA provide no oil repellency even at relatively high concentration in solvent. Fluorinated surfactant provides weak soil repellency at very high concentrations in solvent.

15 Test Method - Water Repellency

Polyester and cotton test cloths of 4.0cm by 4.0cm were used.

- 20 The polyester was pre-treated with 1N Na₂CO₃ and boiled for 15 minutes. It was then washed with distilled water until neutral. It was boiled again in distilled water for 15 minutes after which it was dried in a 65°C oven for 30 minutes.

- 25 The cotton cloth was treated similarly except that it was boiled for 30 minutes with sodium carbonate instead of 15 minutes.

- 27 -

The test cloths were then each immersed in an ethanol solution of perflouro alkyl glucamide for one hour. The test cloths were dried at 40°C for 30 minuets. Water
5 repellency was measured at room temperature using coloured water. The persistence of a 0.01 ml water droplet on the fabric determined the effectiveness of repellency. If the droplet permeates the fabric quickly, there is no repellency. If the droplets spread slowly, repellency is
10 weak. If the droplet maintains a high contact angle, repellency is high.

Results

Perflouro alkyl glucamides (c)-(h) defined in the oil repellency tests were used. The results at various
 5 concentrations in the ethanol are shown in the Tables 7 - 8 below:

Table 1 Water Repellency on Cotton

Concentration (wt%) in Ethanol	0.05	0.1	0.21
Samples			
c	None	None	None
d	None	None	None
e	None	None	None
f	None	None	None
g	None	None	None
h	None	None	None
Cotton only	None		

10

Table 8 Water Repellency on Polyester

Concentration (wt%) in Ethanol	0.05	0.1	0.21	0.5
Samples				
c	High	High	High	Weak
d	High	High	High	None
e	High	High	High	None
f	High	High	High	None
g	High	High	High	High
h	High	High	High	High
Polyester only	None			

It can be seen that perfluoroalkyl glucamides do not provide water repellency for cotton, but do provide water repellency for polyester at concentrations up to 0.5 weight percent.

5

Test-Stability of N-Alkyl Perfluoroalkyl Glucamides

Samples of N-Alkyl perfluoroalkyl glucamides were stored at room temperature for three years. Stability was assessed
10 by comparing NMR, ESI and IR spectra before and after storage. Good stability of the compounds was demonstrated by these spectra.

Test-Deposition of the N-Alkyl Perfluoroalkyl Glucamides on 15 Fabric

A detergent solution comprising 0.6 grams of linear alkyl benzene sulfonate, 0.6 grams per litre of sodium tripolyphosphate, 0.3 grams of sodium carbonate and 1.5
20 grams of sodium sulphate at room temperature was prepared. Perfluoroalkyl glucamides were dissolved at a level of 0.1 wt% in this detergent solution.

Test cloths were prepared by the same method as used in the
25 oil and water repellency tests. The cloths were immersed in ten ml of the detergent solution containing 0.1% perfluoroalkyl glucamide at room temperature for 1 hour and then washed under agitation in 200ml of distilled water for ten minutes. The deposition of N-perfluoroalkyl glucamide
30 was assessed by measuring oil repellency after washing and drying.

- 30 -

Tests were repeated for N-alkyl perfluoroalkyl glucamides having alkyl chain lengths from C₁-C₁₀. All showed significant oil repellency on cotton and polyester after washing once with water. The oil repellency did not
5 decrease after washing once more with water. Perfluoroalkyl glucamides deposit well on to fabric and are not easily rinsed off.

CLAIMS:

1. Fabric treatment compositions comprising a
perfluoroalkyl amphiphilic compound of general
5 formula (I).



wherein:

10

R_f is a group of the formula (II):



- 15 where m = an integer in the range 3-12, preferably 6-10, and X is a halogen atom, wherein at least 50% of the halogen atoms X are fluorine atoms and the remainder are chlorine or bromine atoms,

- 20 A is a divalent linking group, and

R is a hydrogen atom or a C_1 - C_{18} alkyl or alkenyl group.

- 25 2. A fabric treatment composition according to claim 1, wherein the perfluoroalkyl group R_f is of general formula $C_qF_{2q+1}-$ or $C_qF_{2q}Cl-$,

30 wherein q is an integer in the range 3-12, preferably 4-18, more preferably 6-12 and most preferably 8-10.

3. A fabric treatment composition according to claim 1 or 2, wherein the divalent linking group A is selected

- 32 -

- from C₁-C₁₈ (optionally substituted) alkylene, 1,4 phenylene, 1,4 phenylene substituted with at least one group selected from alkyl, alkoxy, F or SO₃Na, the C₁-C₁₈ alkenyl chains or 1,4 phenylene chains being optionally interrupted by -O-.
- 5
4. A fabric treatment composition according to any preceding claim, selected from fabric wash compositions, fabric conditioning compositions, compositions for both washing and conditioning fabrics and non-detergent based fabric care compositions.
 - 10
 5. Use of a perfluoroalkyl amphiphilic compound according to general formula (I) according to claim 1, in a method of cotton fabric treatment, to give oil and soil repellency to the cotton fabric.
 - 15
 6. Use of perfluoroalkyl amphiphilic compound according to general formula (1) according to claim 1, in a method of polyester fabric treatment, to give oil, soil and water repellency to the polyester fabric.
 - 20
 7. A method of treating fabric comprising applying a fabric treatment composition comprising a perfluoroalkyl amphiphilic compound of general formula (I) according to claim 1 to the fabric.
 - 25

8. A perfluoroalkyl amphiphilic compound of general formula (III):

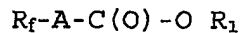


wherein R_f and A have the meanings in relation to general formula I above and R is a C_1-C_{18} alkyl or alkenyl group.

10

9. A method of synthesising the perfluoroalkyl compound of general formula (I) of claim 1, comprising the step of reacting with N-alkyl glucamine a compound of general formula (IV):

15



Wherein R_f and A have the meanings given in relation to general formula I above and R_1 is an alkyl group.

20

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/06376

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 D06M13/408 C11D3/00 C11D1/00 C07C231/02 C07C233/18 //D06M101:06,D06M101:32														
According to International Patent Classification (IPC) or to both national classification and IPC														
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 D06M C11D C07C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, CHEM ABS Data														
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category *</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>EP 0 255 443 A (ATTA) 3 February 1988 (1988-02-03) cited in the application example 24</td> <td>1-4,8,9</td> </tr> <tr> <td>X</td> <td>EDWARDS C M ET AL.: "Novel fluorosurfactants for perfluorochemical emulsification" ADVANCES IN EXPERIMENTAL MEDICINE AND BIOLOGY, SPRING ST., NY, US, vol. 428, 1997, pages 489-493, XP001041396 figure 2, formula P1</td> <td>1-4,8</td> </tr> <tr> <td>A</td> <td>EP 0 375 610 A (CIBA GEIGY AG) 27 June 1990 (1990-06-27) page 1, line 25 - line 51 -/--</td> <td>1-9</td> </tr> </tbody> </table>			Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	EP 0 255 443 A (ATTA) 3 February 1988 (1988-02-03) cited in the application example 24	1-4,8,9	X	EDWARDS C M ET AL.: "Novel fluorosurfactants for perfluorochemical emulsification" ADVANCES IN EXPERIMENTAL MEDICINE AND BIOLOGY, SPRING ST., NY, US, vol. 428, 1997, pages 489-493, XP001041396 figure 2, formula P1	1-4,8	A	EP 0 375 610 A (CIBA GEIGY AG) 27 June 1990 (1990-06-27) page 1, line 25 - line 51 -/--	1-9
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.														
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family														
Date of the actual completion of the international search		Date of mailing of the international search report												
11 December 2001		20/12/2001												
Name and mailing address of the ISA European Patent Office, P.B. 5518 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Fiocco, M												

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/06376

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	EP 0 240 601 A (HOECHST AG) 14 October 1987 (1987-10-14) cited in the application page 4, line 34 - line 43 -----	1-9

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Information on patent family members

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